Environmental Pollution 257 (2020) 113603

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Spatial-temporal distribution and transport flux of polycyclic aromatic hydrocarbons in a large hydropower reservoir of Southeast China: Implication for impoundment impacts☆

Yuling Wu, Xinhong Wang*, Miaolei Ya, Yongyu Li, Yihao Liu, Hanzhe Chen

State Key Laboratory of Marine Environmental Science, College of the Environment and Ecology, Xiamen University, Xiamen, 361102, China

ARTICLE INFO

Article history:
Received 17 March 2019
Received in revised form
8 November 2019
Accepted 8 November 2019
Available online 9 November 2019

Keywords:
Polycyclic aromatic hydrocarbons
Spatial and temporal distribution
Impoundment flux
Hydropower reservoir
Mingjiang river

ABSTRACT

In order to investigate the impacts of dam-related water impoundment on the spatial-temporal variations and transport of anthropogenic organic pollutants, 15 priority polycyclic aromatic hydrocarbons (PAHs) were analyzed in water samples from the Shuikou Reservoir (SKR) of the Minjiang River. The SKR was formed after the construction of the Shuikou Dam, which is the largest hydropower station in Southeast China. The water samples were collected from the backwater zone of the SKR, in both the wet and dry seasons, corresponding to the drainage and impoundment periods of water flow, respectively. The concentrations of the dissolved PAHs in surface water from the wet season (average of 161 ± 97 ng L^{-1}) were significantly higher (ANOVA, $p < 0.01$) than those from the dry season (average of 43 ± 21 ng L^{-1}). PAH concentrations in the SKR decreased from upstream (industrialized cities) to downstream (rural towns or counties), indicating high PAH loads caused by intensive urbanization effects. The high proportions of 3-ring PAHs in the wet season were from local sources via surface runoff; while the elevated proportions of 4- to 6- ring PAHs in the dry season reflected atmospheric deposition emerged of these PAHs and/or volatilization of 3-ring PAHs enhanced. Molecular diagnostic ratios of PAH isomers in multimedium and principal component analysis indicated that PAH presence in the SKR was mainly attributed to pyrogenic origin. The isomeric ratios of fluoranthene to fluoranthene plus pyrene in the wet season were homogeneous, implying that there were continuous new inputs along the riverine runoff. However, these ratios showed spatial downward trend in the dry season, indicating continued degradation of PAHs occurred along the transport path during the impoundment period. The input and output fluxes of PAHs in the SKR were 5330 kg yr^{-1} and 2991 kg yr^{-1}, revealing that the reservoir retained contaminants after impoundment of the hydropower dam.

1. Introduction

Large numbers of blocking dams on rivers have been built around the globe over the past century, a result of the need for water resources for drinking, crop production, and power generation (Rosenberg et al., 2000). Dams also provide a great measure of water control that could help prevent flooding and improve conditions for shipping (Brown et al., 2008). Although the dams have great economic benefits for human beings, the water impoundments of the dam-related reservoirs also have brought negative impacts on the river eco-environment and human health (Chao et al., 2008). Dam-related impoundments change the hydrological conditions, and then turn the dammed reaches of the natural flowing rivers into human-made lacustrine regimes (Wei et al., 2016). In particular, damming could lower river water flow velocity, alter stream nutrient cycling, induce algal blooms, support the build-up of silt, block fish migration route, and overall degrade aquatic resources (Campbell et al., 1998; Vörösmarty et al., 2003; Morais et al., 2009; Wang et al., 2009; Dang et al., 2010). Moreover, impoundments by river dams have also been shown to result in accumulations of anthropogenic pollutants in the reservoirs (Audry et al., 2010; Deyerling et al., 2014). Therefore, under the changed hydrodynamic conditions in the reservoirs, the impacts of water impoundment on biogeochemical processes of pollutants are critical human health problems that require more research to better

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

* Corresponding author.College of the Environment and Ecology, Xiamen University, Xiamen, 361102, China.
E-mail address: xhwang@xmu.edu.cn (X. Wang).

https://doi.org/10.1016/j.envpol.2019.113603
0269-7491/

manage water resources (Wu et al., 2004).

Polycyclic aromatic hydrocarbons (PAHs) are a group of priority organic pollutants of critical environmental and public health concern. This is a result of their toxic, mutagenic and carcinogenic potential to ecosystem and humans (Gonzalez-Gaya et al., 2019). The extensive anthropogenic activities (e.g., incomplete combustions of fossil fuel and biomass, petroleum seeps during industrial and agricultural production processes) have resulted in ubiquitous occurrence of PAHs in the environment (Wang et al., 2007; Li et al., 2016). PAHs can enter the aqueous environment mainly via atmospheric deposition, surface runoff, municipal/industrial effluents, or oil leakage (Countway et al., 2003). With tremendous economic development and high energy consumption over the past few decades, China has been regarded as a large emitter of PAHs into the world's ecosystems (Xu et al., 2006; Lang et al., 2008). The occurrence, source, and ecological risk to ecosystems of PAHs in natural water environments of China have been extensively studied (Li and Duan, 2015; Du and Jing, 2018; Meng et al., 2019). In China, the water conservancy and hydropower projects continue to develop at increasing rates in major rivers (e.g., Yangtze River, Yellow River, Pearl River, and others). It was reported that China had built 98,795 reservoirs of various types according to the 2017 Statistic Bulletin on China Water Activities (Ministry of Water Resources of the People's Republic of China, 2018). With these developments, PAH pollution in the reservoirs further threaten ecological security and drinking water quality have been increasing attentions, such as in the Three Gorges Reservoir (Wang et al., 2012; Deyerling et al., 2014; Wang et al., 2016; Lin et al., 2018), Guanting Reservoir (Wang et al., 2004), Fenhe Reservoir (Tian et al., 2013), Dahuofang Reservoir (Lin et al., 2012, 2013b) and Mopanshan Reservoir (Liu et al., 2013).

The Minjiang River is the largest river in Fujian Province, Southeast China and highly disturbed by anthropogenic activities (such as large emissions of industrial and municipal wastewater, frequent shipping, constructions of cascade hydropower stations) (Zhang et al., 2004) (Fig. 1a). The Shuikou Reservoir (SKR) is located in the middle reach of the Minjiang River due to the construction and impoundment of the Shuikou hydropower station since 1993. This hydropower station is the largest one in Southeast China, the water impoundment of this dam has altered hydrologic conditions and thus created numerous environmental problems. The SKR is also subjected to numerous anthropogenic influences that challenge its susceptive ecosystem in recent years. Frequent water eutrophication and depleted aquatic biodiversity of the SKR occurs caused by increased emissions of pollutants and nutrients from surrounding cities (Chen et al., 2012). The increasing environmental pollution of the SKR directly affect the drinking water safety of tens of millions of people in the downstream Minjiang River. However, available information is lacking for understanding the impoundment impacts on the biogeochemical processes (e.g., occurrence, transport and fate) of anthropogenic organic pollutants (such as PAHs) in the SKR. Whether the hydropower dam would result in the pollutant entrapment in the SKR is also an open question.

This study aims to: (1) determine the levels and possible sources of PAHs in water of the SKR from the wet and dry seasons, (2) elucidate the temporal and spatial variations of PAH concentrations and compositions in the artificial reservoir during drainage and impoundment periods; and (3) evaluate the annual impoundment flux of PAHs transported in the reservoir river. The purpose of this study was to provide effective early warning for regional water resources and protection of human health.

2. Materials and methods

2.1. Study area

The Minjiang River has a mainstream length of 562 km with a drainage area of 60,992 km^2. It is located in the subtropical monsoon zone with an annual precipitation of 1800–2200 mm, and its annual average riverine runoff is 610×10^8 m^3, with 71%–80% being discharged in the wet season (April to September) and 20%–29% in the dry season (October to next March). The Shuikou hydropower station is the last level of the cascade hydropower stations in the Minjiang River, it has provided electric power generation, navigation for shipping, flood prevention, aquaculture, tourism, and irrigation. The Shuikou Dam is ~870 m in length and 101 m in height. It limits the water level to 61 m during the flood season (April to July), at 65 m for a normal water level with water volume of 23.4×10^8 m^3 (August to November and the February to March), and generally fluctuates to 57 m during the dry season (December to next January). The SKR is between the sections of Yanping District of Nanping City and Minqing County of Fuzhou City

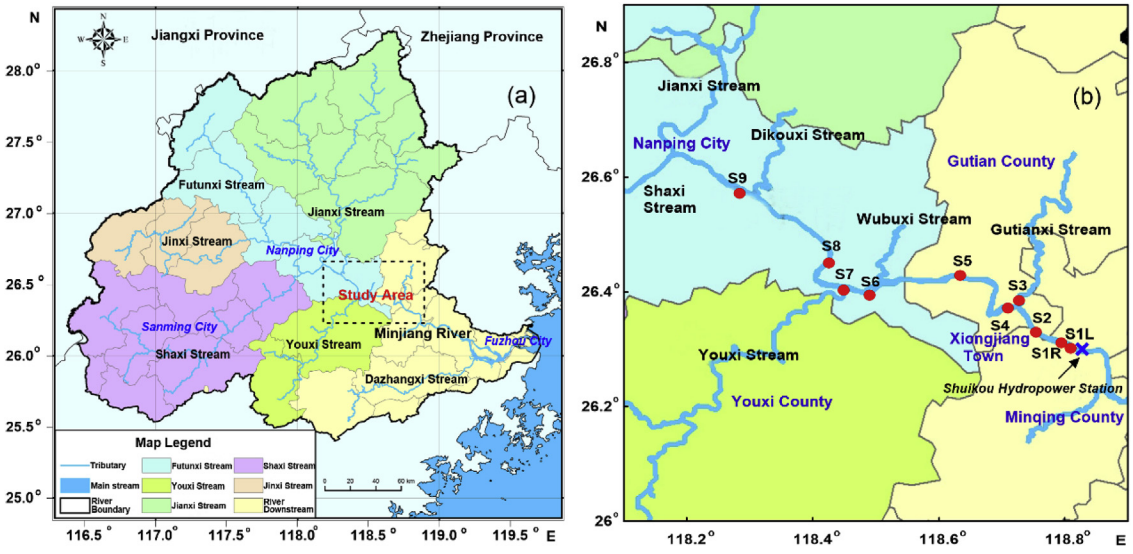

Fig. 1. Map of study area (a) and sampling stations (b) in the SKR of the Minjiang River.

(N26°18.198′-26°38.417′, E118°10.733′-118°48.729′) (Fig. 1). The length of the main SKR is 94 km and the control area is 52 438 km^2, accounting for 86% of the total area of Minjiang River watershed. Three tributaries (Futunxi Stream, Shaxi Stream, and Jianxi Stream) of the upper reach flow through Nanping then converge into the SKR area (Fig. 1). When the water level is 65 m, the backwater zone can reach to the Shaxi stream dam, which is 108 km to the Shuikou dam, when the water level is 57 m, the backwater zone fluctuates to the mouth of Jianxi stream, which is 11 km to Shaxi stream dam. As expected, there was statistically significant seasonal variations of water levels in the backwater zone (Supplementary Information (SI) Fig. S1). Due to the river water flows slowly in the SKR, the fish cage cultures develop rapidly in the reservoir and they become a major freshwater fish farm in Fujian Province.

2.2. Sample collection and organic analysis

Water samples at ten sampling stations along the SKR of the Minjiang River were collected in the wet season (June 2014, summer, drainage period) and dry season (January 2015, winter, impoundment period). All stations were in the backwater zone, relevant information about each of the sampling stations are illustrated and noted in Figs. 1b and SI Table S1. Surface water (<0.5 m, below water surface) was directly collected from the river using stainless steel barrels. Bottom water (<1 m, above water bottom) was collected using a polyvinyl chloride (PVC) water sampler. Water samples were stored in 4 L pre-cleaned brown glass jars, and then were immediately filtered through pre-combusted glass fiber filters (GFFs) to obtain suspended particulate matter (SPM) containing particulate organics. After that, the dissolved organics in the filtered water samples were extracted through pre-conditioned solid phase extraction (SPE) cartridges spiked with deuterated PAHs as surrogates. Synchronously, aerosol sampling in the wet season was carried out for three days in Nanping and Minqing. Total suspended particulates (TSP, particle phase) and gaseous phase for aerosol samples were collected using pre-combusted quartz fiber filters (QFFs) and pre-cleaned polyurethane foams (PUF), respectively. Three rainwater samples in the wet season were also synchronously collected for one day in Minqing, and they were directly trapped by spiked SPE cartridges.

The analysis procedures for GFFs and SPE cartridges from river water and rainwater samples, and QFFs and PUF from aerosol samples are described in our previous papers (Wu et al., 2011; Ya et al., 2017a; b, 2018). Details of sample pretreatment and instrumental analysis using Agilent 6890 Series gas chromatography Agilent 5973 mass spectrometry are described in the SI Text S1 and S2. The following 15 priority PAHs (without naphthalene, Nap) designated by the US EPA were analyzed: acenaphthylene (Ace), acenaphthene (Acen), fluorene (Flu), phenanthrene (Phen), anthracene (An), fluoranthene (Fluo), pyrene (Py), benzo(a) anthracene (BaA), chrysene (Chry), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IP), benzo(g,h,i)perylene (BghiP) and dibenzo(a,h) anthracene (DBA).

2.3. Quality assurance and quality control

The concentrations of PAHs in this study were quantified by internal standard method. Laboratory spiked blanks and replicate samples were analyzed along with field samples. Target compounds in blanks were 1–2 orders of magnitude less than the field water samples (SI Table S2), which meant the relatively low background or contamination of PAHs during pretreatment process. The linearity coefficients (R^2) of standard curve were 0.9613–0.9932 (1 ppb–2 ppm, n = 10). The method recoveries of 15 PAHs ranged from 74% to 126% in the dissolved phase, and 60%–120% in the particulate phase (SI Table S2). The method detection limits (MDLs) were calculated as the mean plus three times the standard deviation of the method blanks (n = 7), MDLs of 15 PAHs ranged from 2×10^{-3} to 8×10^{-3} ng L^{-1} in the dissolved phase, and 2×10^{-3} to 7×10^{-3} ng L^{-1} in the particulate phase (SI Table S2). The labeled peaks of target compounds for authentic PAH standards at about 10 times of the MDLs and one field water sample are displayed in SI Fig. S2.

3. Results and discussion

3.1. Levels and ecological risk assessment of PAHs

In the wet season, the concentrations of dissolved PAHs in surface water from the SKR ranged from 19 to 303 (average of 161 ± 97) ng L^{-1}, which were about 25 times higher than particulate PAHs (3.4–15 ng L^{-1}, average of 6.5 ± 3.3 ng L^{-1}) (SI Table S3). The percentages of particulate PAHs in total PAHs (dissolved phase plus particulate phase) ranged from 1.7% to 29% (average of 7.0 ± 8.6%). In the dry season, the concentrations of dissolved PAHs in surface water from the SKR ranged from 22 to 86 (average of 43 ± 21) ng L^{-1}; and the concentrations of dissolved PAHs in the bottom water (67–123 ng L^{-1}, average of 89 ± 24 ng L^{-1}) from sites S3 to S1 close to the hydropower station were much higher than those in surface water (22–44 ng L^{-1}, average of 28 ± 11 ng L^{-1}) (SI Table S3). Compared with the major rivers in China (e.g., the Yellow River, Yangtze River, Pearl River, etc.) and other countries (e.g., the Ganges River in India, Nile River in Egypt, the Mississippi River and Susquehanna River in USA, etc.) (SI Table S4), the PAH concentrations in this study are comparable to or lower than those in China and USA but are much lower than lower than those in India. Therefore, the level of PAHs in water from the SKR was at a low-middle point of the global range, the PAH contamination in the wet season was more prominent, especially in the upstream SKR.

The dissolved organic contaminants are precisely proportional to their chemical activity, e.g., bioavailability and bioaccumulation in organisms (Reichenberg and Mayer 2006). Therefore, the concentrations of organic contaminants in the dissolved phase are more ecologically relevant in water quality monitoring and evaluation of the potential adverse effects on organisms than the total environmental concentrations (Carls et al., 2008; Prokeš et al., 2012). In this study, the risk evaluation of dissolved PAHs in the water environment follows the water quality standards developed by the environmental protection ministries. The concentrations of dissolved BaP (Wet season: 0.07–0.29 ng L^{-1}, Dry season: below detection limit) of the SKR were below the environmental quality standard for surface water (GB3838-2002) as established by the State Environment Protection Agency of China (SEPA) (<2.8 ng L^{-1} for BaP) (SEPA of China, 2002). However, the BaP concentration in water should be less than 0.12 ng L^{-1} for consumption both of water and organism according to the national recommended water quality criteria for human health established by US EPA (US EPA, 2015). As established by the European Union Commission (EUC), the annual average environmental quality standard for BaP should be less than 0.17 ng L^{-1} that could pose a significant risk to the environment or human health in inland surface waters (EUC, 2013). BaP concentrations in the dissolved phase of the SKR from the wet season were slightly higher (sites S9 to S7) than or close (sites S6 to S1) to the required range (<0.12 or 0.17 ng L^{-1}) of the guideline values of US EPA and EUC (SI Fig. S3). This means that BaP residues in water of the SKR did not meet the requirements of US EPA and EUC. Besides, the desorption of particulate PAHs to the dissolved phase might increase the ecological risk of BaP (SI Fig. S3), so PAHs

in the SKR inevitably present some latent eco-environment risks.

3.2. Seasonal and spatial variabilities of PAHs

3.2.1. PAH concentrations

The concentrations of dissolved PAHs in surface water of the SKR from the wet season were significantly higher (ANOVA, $p < 0.01$) and changed more sharply than those from the dry season (Fig. 2). In general, the frequent rainfall events during the wet season caused strong surface runoff and heavy wet deposition, which could introduce terrestrial and atmospheric PAHs to water bodies (Ngabe et al., 2000; Zhu et al., 2004; Gigliotti et al., 2005; Del Vento and Dachs, 2007). As mentioned above, more than 70% of the riverine runoff in the Minjiang River is discharged in the wet season, and the precipitation in 2014 was 1350 mm with more than 70% of the rainfall during the wet season (SI Table S5). Hence, the large volume of water discharge in the wet season led to the high concentration of dissolved PAHs enriched in the reservoir region. Furthermore, frequent impoundment of the SKR lowers water flow that might increase exposure of dissolved PAHs to photo-degradation in the upper layer of water (Tobiszewski and Namieśnik, 2012; Katsoyiannis and Breivik., 2014). In addition, human activities (such as larger emissions of municipal sewage, urban runoff and frequent shipping) are more intense in summer, which cause the higher concentrations of anthropogenic PAHs in the wet season.

Spatially, the concentrations of dissolved PAHs in surface water from the SKR decreased gradually from upstream to downstream both in the wet and dry seasons (sites S9 to S2), and their variation trends also were fairly similar ($r = 0.80$, $p < 0.01$, Pearson correlation) (Fig. 2a). The old heavy industrial areas of Fujian Province (e.g., Sanming City and Nanping City) are also located in the upstream SKR, where large amounts of industrial wastewater discharge into the tributaries (especially Shaxi Stream) (Xu et al., 2014). As the conjunction of the tributaries, the water pollution in Nanping section of the Minjiang River is particularly high. Meanwhile, the large-scale animal husbandry and rural non-point sources in Nanping City and Sanming City also release pollutants to the SKR. The high PAH concentrations were also found at site S7, suggesting that the tributary-Youxi Stream has a proportionally large contribution of PAH pollution to the mainstream of the Minjiang River. The decreased trends of PAH concentrations from the industrialized cities (upstream) to town or county areas (downstream) were subjected to regional anthropogenic influences (e.g., industrial, domestic and agricultural wastewater discharges). As a result of the natural photo- or bio-degradation, and reduced inputs of pollutants, PAH concentrations decreased in the downstream reservoir. The blooming water hyacinth (*Eichhornia crassipes*) in the downstream SKR may be an important biological carbon pump that transfers organic pollutants from water to sediment (Chen et al., 2012). The self-cleaning capacity of dissolved PAHs in the SKR was found to be strong since PAH concentration reduced drastically by more than half from upstream to downstream. The responsible processes are thought to be dilution, degradation or deposition of PAHs adsorbed to organism debris and particles under the low flow rate (Deyerling et al., 2014)). This hypothesis could be further supported by data showing higher concentrations of dissolved PAHs in the bottom water than in surface water (SI Table S3). It should be noted that PAH concentrations increased a little at the stations close to the Shuikou hydropower dam (sites S1L and S1R) (Fig. 2), suggesting that the dam might support contaminant retention or accumulation. This phenomenon was more significant in the particulate PAHs of the wet season (SI Fig. S4).

3.2.2. PAH compositions

According to the number of aromatic rings, the 15 priority PAHs were divided into 2 groups: low molecular weight (LMW) PAHs (3-ring PAHs) chiefly originated from a low- or moderate-temperature combustion process (such as biomass burning and domestic coal burning); and high molecular weight (HMW) PAHs (4- to 6- ring PAHs) mainly ascribed to the high-temperature combustion process (such as vehicle exhaust and industrial coal combustion) (Mai et al., 2003). In the wet season, all of the targeted compounds were detected in both dissolved and particulate phases of water samples (SI Table S3). LMW-PAHs (i.e., Ace, Acen, Flu, Phen, and An) dominated the dissolved PAH assemblages at all sampling stations, these accounted for 85%–94% (except site S2) of the total PAHs, with Flu ($39 \pm 6.9\%$) and Phen ($25 \pm 11\%$) being the most abundant (Figs. 2b and SI Fig. S5a). In contrast, HMW-PAHs such as 4-ring compounds (i.e., Fluo, Py, BaA, and Chry) accounted for 5.5%–15% of the total dissolved PAHs, and the suspected carcinogenic 5- to 6-ring PAHs (i.e., BbF, BkF, BaP, IP, BghiP, and DBA) had very low concentrations at all sampling stations, accounting for 0.23%–1.4% of the total dissolved PAHs (Figs. 2b and SI Fig. S5a). Flu ($23 \pm 25\%$) and Phen ($33 \pm 34\%$) were also the most dominant compounds in the particulate PAHs from the wet season (SI Fig. S5b). In the dry season, LMW-PAHs accounted for 50%–70% of the total dissolved PAHs in surface water with Phen ($31 \pm 2.7\%$) being the most abundant (Figs. 2b and SI Fig. S5c). For HMW-PAHs, 4-ring compounds of accounted for 30%–49% of the total dissolved PAHs with Fluo ($16 \pm 4.2\%$) and Py ($18 \pm 4.9\%$) being the most abundant; and a majority of 5- to 6-ring compounds were below detection limits or

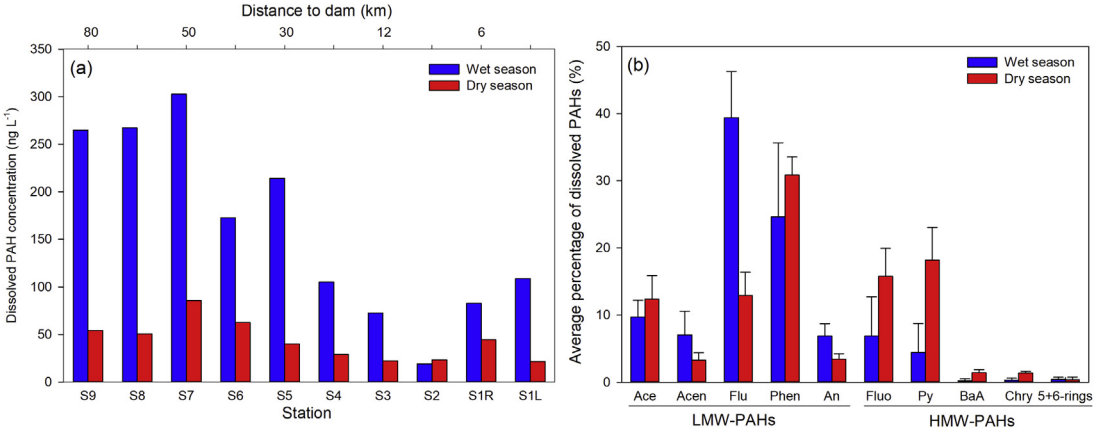

Fig. 2. Concentrations and compositions of dissolved PAHs in different seasons.

had low concentrations accounting for not detected to 1.1% of the total dissolved PAHs (Figs. 2b and SI Fig. S5c). Generally, LMW-PAHs (especially Phen) were the most abundant components in both seasons (SI Figs. S5 and S6), which could be explained from the relatively high water solubility of LMW-PAHs (Tsapakis et al., 2003). The predominant LMW-PAHs (>80%, especially Phen) in gaseous phase of aerosol samples (SI Figs. S5d and S6d), which were similar to those in the dissolved phase also reflected air-water exchange (net deposition flux) that could be responsible for LMW-PAHs in surface water (Chen et al., 2016; Wu et al., 2019).

Spatially, the percentages of the dominant compounds changed significantly (from sites S9 to S3) in the wet season, with Flu having increased from 34% to 53%, Phen decreased from 37% to 12% (SI Fig. S5a). Different from the other stations, the PAH composition at site S2 in the wet season was dominated by Flu, Fluo, Py and Acen, and the percentages of 3-ring and 4-ring PAHs accounted for 56 and 43% of the total PAHs, respectively. Site S2 is close to the Town of Xiongjiang, a region known for the cage culturing, so densely distributed fish cages and frequent aquaculture activities may change the input features and degradation of PAHs. In the dry season, from upstream to downstream (except S1L and S1R), the percentages of the most dominant Phen and Fluo decreased from 37% to 27%, and 23%–9.5%, respectively; while the percentages of Flu and Py increased from 7.7% to 20%, and 11%–19%, respectively (SI Fig. S5c). The changing PAH compositions in both seasons might be related to changing sources or selective degradation occurred during fluvial transport processes (Lin et al., 2013a; Katsoyiannis and Breivik., 2014).

Surface water in the wet season was relatively enriched in LMW-PAHs but depleted in HMW-PAHs compared with those in the dry season (SI Fig. S6). This could be explained by enhanced water solubility of atmospheric LMW-PAHs at a relatively higher temperatures in the wet season than in the dry season (Luo et al., 2008). Although PAH compositions in surface water from the wet season were quite different from that of rainwater samples (SI Figs. S5d and S6d), dominant LMW-PAHs were found in soils collected along the banks of the Minjiang River (Sun et al., 2016). This indicated that surface runoff containing eroded soil caused by wet deposition in the wet season might be contributing to the presence of PAHs in surface water. Therefore, we inferred that wet deposition-related processes in the wet season were the vital input pathways of PAHs entering into the Minjiang River. Compared with the wet season, the proportions of LMW-PAHs decreased (especially Flu), but HMW-PAHs increased significantly (especially Fluo and Py) in the dry season. This could be explained by enhanced vaporization and weakened water solubility of LMW-PAHs at relatively lower temperature in the dry season (Luo et al., 2008). This illustration could be supported by observations of higher proportions of LMW-PAHs in bottom water (80%) than in surface water (62%) during the dry season. Furthermore, majority of gaseous PAHs with moderate to high molecular weight (especially Phen, Fluo and Py) exhibited a net deposition (air-to-water) through air-water exchange in winter, which could also cause increased proportion of HMW-PAHs in surface water from the dry season (Qin et al., 2013). Previous studies also found that dry deposition fluxes of atmospheric PAHs contributed to surface water in winter was significantly higher than those in summer (Lang et al., 2002; Jiang et al., 2018). And the fine particles (0.1–1 μm) with high concentrations of HMW-PAHs were the predominant components of atmospheric dry deposition (González-Gaya et al., 2014; Ren et al., 2017). The high proportions of HMW-PAHs in TSP were also found although these samples collected in the wet season (SI Fig. S6), further indicating that PAHs in water contributed by direct atmospheric deposition in the dry season might be more important.

3.3. Possible sources and transport of PAHs

3.3.1. Molecular diagnostic ratios

Molecular diagnostic ratios (MDR) of PAHs (See SI Table S6) are widely used to distinguish natural and anthropogenic sources, or pyrolytic and petrogenic anthropogenic sources (Yunker et al., 2002; Tobiszewski and Namieśnik, 2012). PAH ratios suggest that the input sources were different between the wet season and dry season (Fig. 4 and SI Table S6). In the wet season, An/(Phen + An) ratios at all stations were >0.1, Fluo/(Fluo + Py) ratios at all stations were >0.5, and BaA/(BaA + Chry) ratios (except site S1R) were above 0.35. In the dry season, An/(Phen + An) ratios at most stations is less than or about 0.1, Fluo/(Fluo + Py) ratios were above 0.4 (except sites S3 to S1), and BaA/(BaA + Chry) ratios at all stations were >0.35 (Fig. 3 and SI Table S6). These findings indicate that the presence of PAHs in water of SKR was mainly caused by pyrogenic origins (fossil fuel and/or biomass combustion), accompanied by minor inputs from petroleum contamination (See SI Table S6).

The ratios of An/(An + Phen) and Fluo/(Fluo + Py) in the dry season were lower than in the wet season (Fig. 4). Besides of the source shifts along the transport paths during different seasons (Lin et al., 2013a), the selective photo- or bio-degradation of PAH isomers due to the prolonged exposure to the environment might be resulting in significant alteration of the MDR (Tobiszewski and Namieśnik, 2012; Lin et al., 2013a; Katsoyiannis and Breivik., 2014). Photo-degradation of An is faster than its isomeric Phen (Tobiszewski and Namieśnik, 2012; Katsoyiannis and Breivik., 2014), and Fluo has been reported to be less persistent than Py in the environment (Yu et al., 2005). Therefore, higher ratios in the wet season might represent fresh sources of pyrogenic PAHs from local inputs. However, the lower ratios in the dry season may be attributed to long-range transport of PAHs, which was related to slow fluvial transport of pollutants during the impoundment period of the SKR, or the elevated atmospheric deposition resulting from the influence of Asian monsoon. For further proof, we also combined the composition patterns and MDR of PAHs in aerosol and rainwater samples to further explore the input pathways of PAHs in water of the SKR (Fig. 3, S4-5 and SI Table S6). Though the data are difficult to interpret based on the composition patterns, the MDR of PAH isomers in the wet season were closer to the value of rainwater and PUF samples (SI Table S6). Therefore, PAHs in the wet season were mainly transferred into the river water via domestic sewage discharge, rainfall induced soil erosion and atmospheric wet deposition. However, the MDR of PAH isomers in the dry season were relatively close to the values of TSP samples from Nanping and Minqing (SI Table S6). It was thus inferred that atmospheric dry deposition (e.g. fossil fuel combustion from industrial, mining production and traffics) dominated in the dry season (Zhang et al., 2012).

The ratios of Fluo/(Fluo + Py) were relatively stable in the wet season (Fig. 4), which means that there were continuously new inputs of PAHs along the river (Lin et al., 2013a). In the dry season, the ratios of Fluo/(Fluo + Py) gradually decreased (Fig. 4), with no obvious additional sources along the transport path. The explanation offered for this change may be more degradation of selected congeners during the transport, reflecting a normal transport process in river systems (Katsoyiannis and Breivik, 2014). In general, the significant seasonal and spatial variations of Fluo/(Fluo + Py) ratios suggested that the compositions of Fluo and Py are more susceptible to changes during transport process than the other two ratios. In addition, it's interesting to note that, under the disturbances the tributaries of Youxi Stream and Gutianxi Stream

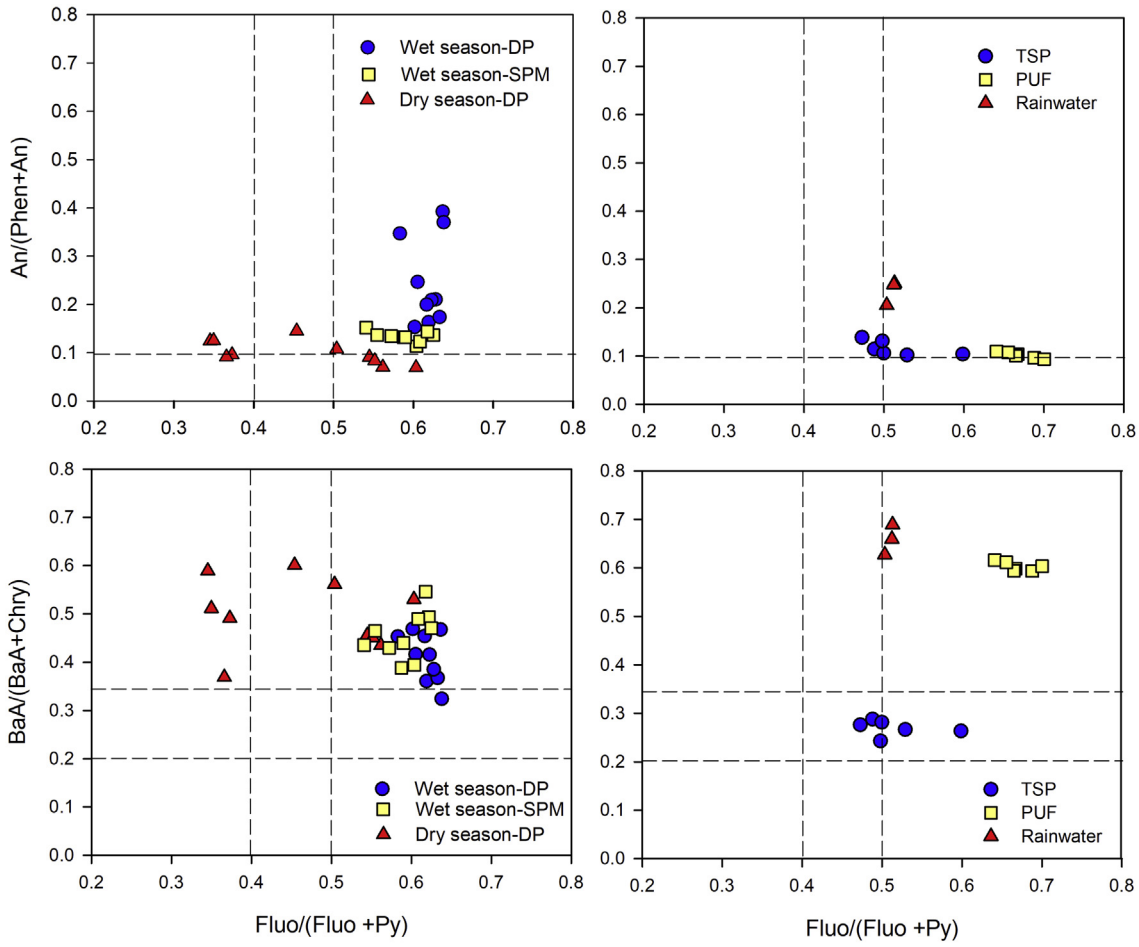

Fig. 3. Plots of PAH isomer ratios in water, aerosol and rainwater (DP: dissolved phase).

discharging into the SKR, the broken trends (dramatic increase or decrease) of PAH ratios from sites S4 to S3 then to the Shuikou Dam were found, while the fluctuations of PAH ratios at site S7 were less obvious. Although there are large cascade hydropower stations located in the Youxi Stream and Gutianxi Stream, the average river slope of the Gutianxi Stream (6.6‰) is higher than the Youxi Stream (2.0‰). Therefore, the flood drainage (especially in the wet season) with higher river slope regulated by the large hydropower station could cause stronger fluvial erosion from the tributaries, this might disturb the normal fluvial transport of river materials in the SKR. This is consistent with the higher concentration of particulate PAHs at sites S7, S3 and S2 in the wet season (SI Fig. S4). Overall, the water impoundment significantly changed the normal transport processes of PAHs.

3.3.2. Principal component analysis

In order to enhance the reliability of source identification and estimate the relative contributions and site variances of PAHs from specific sources, the principal component analysis with multiple linear regression (PCA-MLR) was conducted on the same dataset in order to identify source profiles and calculate relative contributions of PAHs (SI-Text S3). Two principal components (PCs) were retained in both seasons (Fig. 5a and b). In the wet season, PC1, responsible for 48% of the total variance, is predominantly weighted by relatively higher molecular weight PAHs (BaA, Chry, and 5- to 6- ring PAHs) (Fig. 5a). The HMW-PAHs (such as BaP, IP and BghiP) are indicators of vehicle exhaust (gas- and diesel-powered vehicles) (Ravindra et al., 2008). Thus, PC1 might be related to direct traffic fuel emissions or light fossil fuel combustion. PC2, contributed 44% of the total variance in the wet season, is heavily weighted by relatively low molecular weight PAHs (3-ring PAHs, Fluo, and Py); reported to be related to coal and biomass combustion (Larsen III and Baker, 2003; Zhang et al., 2012). In the dry season, PC1, accounting for 37% of the total variance, is predominantly loaded with BbF and BkF with moderate loadings of Py and Chry (Fig. 5b), which can be identified as the contribution from vehicle emission (Yang et al., 2013). PC2, accounting for 52% of the total variance in the dry season, is heavily weighted in lower to moderate molecular weight PAHs (3-ring PAHs, Fluo, BaA and Py), which can represent the contribution from coal and biomass combustion (Larsen III and Baker, 2003; Ravindra et al., 2008). Based on the calculations from MLR (SI Text S3), the contributions of coal and biomass combustion to total riverine PAHs in the wet and dry seasons were 77% and 61%, respectively, while the contributions of vehicle exhausts were 23% and 39%, respectively. Specifically, the high contribution of vehicle emissions in winter might be related to prominent atmospheric dry deposition (Salim et al., 2019). Overall, a majority of the riverine PAH loadings were ascribed to coal and biomass combustion, qualitatively consistent with the source assessment results based on MDR of PAH isomers. It was clear that the loadings of individual PAHs from PCs were agminated in the wet season, but distributed dispersedly in the dry season, indicating the homogeneous sources of PAHs in the wet season and heterogeneous sources (originate from diverse sources) of PAHs in the dry season. The site-specific

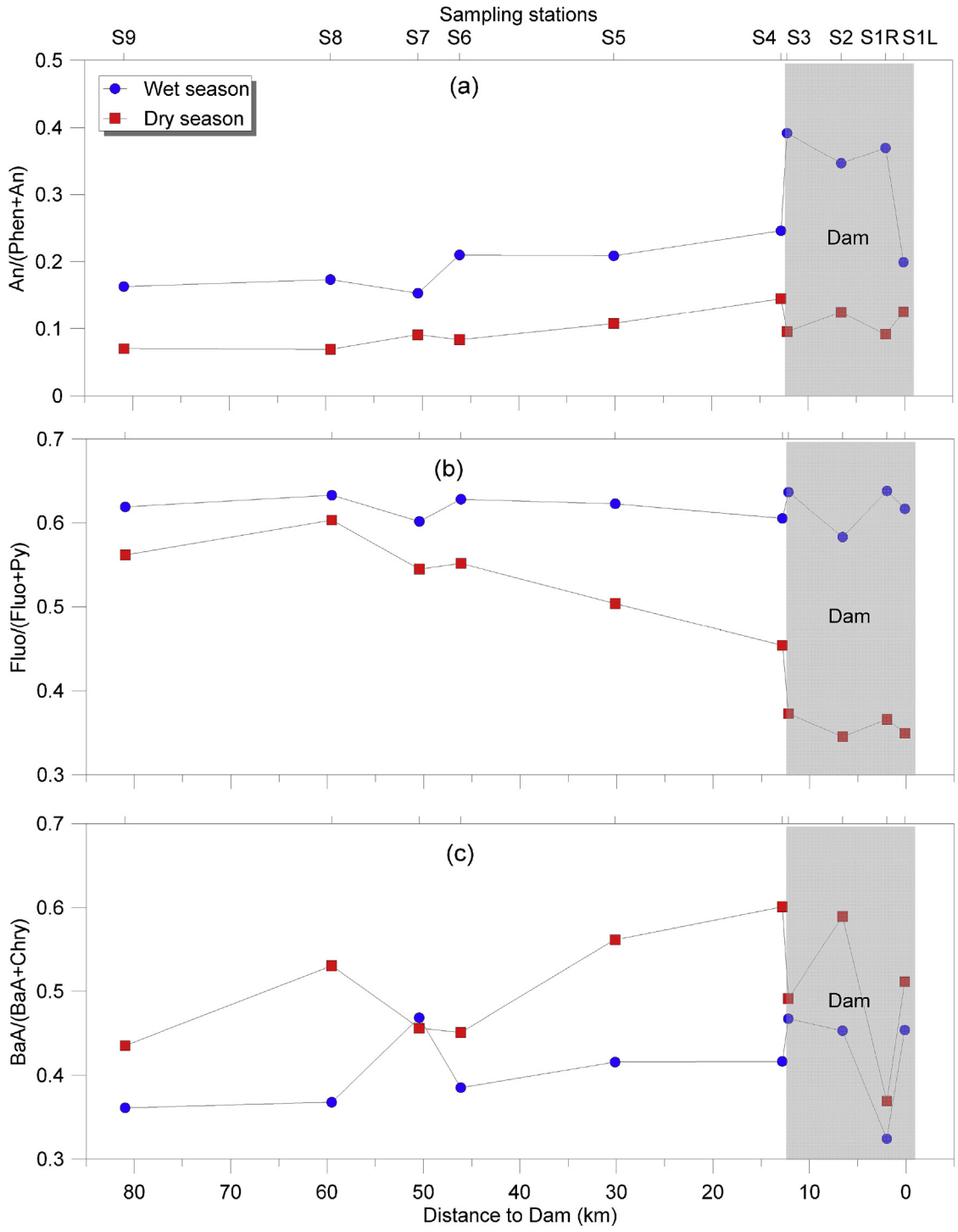

Fig. 4. Molecular diagnostic ratios of dissolved PAHs in different seasons.

scores of PAHs from PC1 and PC2 are presented in Fig. 5c and d. In both seasons, the upstream SKR (sites S9 to S5) was dominated by coal and biomass combustion and then reduced in downstream (sites S4 to S1), where in contrast received contributions from light fossil fuel combustion. The two sources with high contributions appeared at site S7 in both seasons, likely a result of the location near the mouth of the Youxi Stream that receive large amounts of agricultural and domestic sewage discharge. Generally, due to the mixed land uses of agriculture, industrial, residential living of urban and rural areas, and widely distributed fish cage cultures in the SKR, the predominate anthropogenic PAHs with pyrolytic sources displayed distinct spatial transport processes in water of the SKR.

3.4. Estimation for impoundment flux of PAHs

The impoundment, storage and regulation of the river dams influence the river hydrodynamic conditions and the biogeochemical processes of biogenic and anthropogenic materials, the

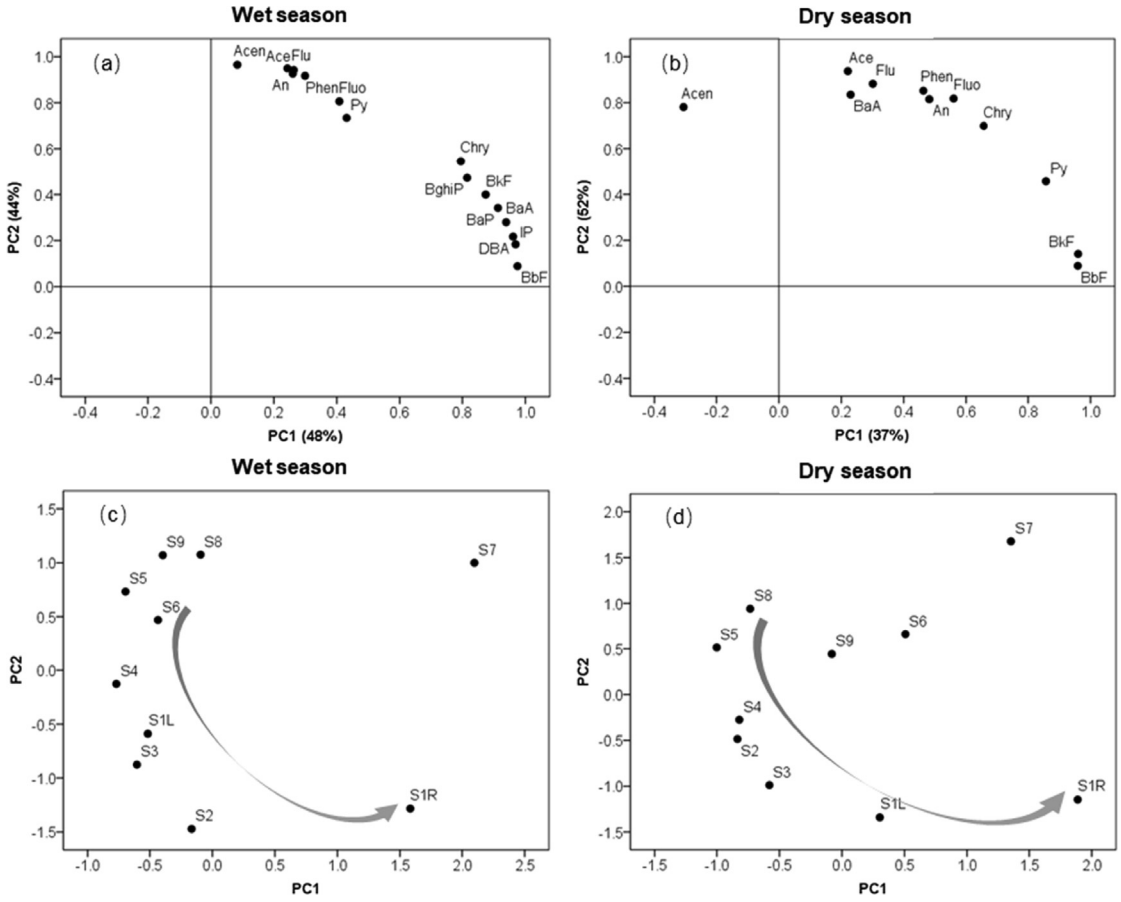

Fig. 5. Plots of loadings (a, b) and scores (c, d) of PAHs from PCA in the SKR.

material fluxes transported to the downstream river also change after the river dammed (Humborg et al., 1997; Wang et al., 2009; Wei et al., 2016). For example, SPM transport to the Yangtze estuary was reduced by more than half compared with the 1970s after operation of the Three Gorges Reservoir in 2003 (Dai et al., 2011); and the annual average sediment discharge from suspended load in the downstream Minjiang River (1993–2006) was reduced to 37% compared with those before the built of the hydropower stations (1951–1975) (Chen et al., 2012). The entrapments of anthropogenic nutrients and pollutants in the reservoir rivers could result in high ecological risks, such as elevated harmful pollutants during dredging water reservoirs (Mwanamoki et al., 2014). Therefore, it is important to estimate the impoundment fluxes of pollutants during transporting through the reservoir rivers. This is also an essential prerequisite for the implementation of total amount control and reducing cross-regional disputes, as well as providing decision-making basis for the pollution control.

In this study, according to the 2014 statistics of inflow and outflow of water discharges in the Shuikou hydropower station (SI Table S7) and the dissolved PAH concentrations in the wet and dry seasons, a preliminary estimation for the input and output fluxes of PAHs in the SKR was conducted, and detailed information is shown in SI Text S4. The input flux of PAHs (5330 kg yr^{-1}) was quite larger than the output flux (2991 kg yr^{-1}) (Table 1), despite that the input water discharge was nearly the same as the output water discharge, the reservoir almost remains amount of dissolved PAHs during transporting processes, and impoundment flux was 2339 kg yr^{-1} which occupied 44% of the input flux of PAHs. Furthermore, the impoundment fluxes of LMW-, HMW-, and total PAHs in the wet season were significantly higher than those in the dry season, and the impoundment ratios of LMW-PAHs were higher than those of HMW-PAHs. The Minjiang River covers nearly half of the area and one third of the population of Fujian province, and it is responsible for the main source for water supply for industrial, agricultural, residential purposes. As the largest reservoir in Southeast China, the SKR in the Minjiang River is crucial for the storage and supply of drinking water for local residents. Therefore, more emphasis on understanding the PAHs entrapment and accumulation in the SKR of the Minjiang River for drinking water security.

Table 1
Impoundment flux (kg yr^{-1}) and ratio (%) of PAHs in the SKR.

PAHs	Parameters	Wet season	Dry season	Annual flux
LMW-PAHs	Influx	4377	354	4731
	Outflux	2350	219	2569
	Impoundment flux	2027	136	2162
	Impoundment ratio	46	38	46
HMW-PAHs	Influx	391	208	599
	Outflux	236	186	422
	Impoundment flux	155	22	177
	Impoundment ratio	40	11	30
Total PAHs	Influx	4768	562	5330
	Outflux	2586	405	2991
	Impoundment flux	2182	157	2339
	Impoundment ratio	46	28	44

4. Conclusions

In the backwater zone from the SKR of the Minjiang River,

significant spatial-temporal variations of PAH concentrations, compositions and sources in water were displayed. PAH concentrations in water of the SKR in the wet season were higher than those in the dry season, and the overall contamination level of PAHs was lightly to moderately polluted, compared to other river systems. The input sources in the SKR were primarily from the upstream urbanized cities and its tributaries, while PAH concentrations declined by more than half from upstream to downstream. The responsible processes for the high self-cleaning capacity are thought to be dilution effect, degradation or deposition of PAHs adsorbed to organism debris and particles. The composition patterns of PAHs were dominated by 3-ring PAHs in both seasons, the relatively high abundance of 4-ring PAHs in the dry season, this dynamic change was related to the seasonal variations in temperature, anthropogenic activities, atmospheric deposition, and impoundment impact. MDR ratios of PAHs and PCA receptor model inferred that PAHs in the SKR were mainly from pyrolytic origin (fossil fuel and/or biomass combustion), the input pathway was the riverine runoff by the discharge of domestic sewage, land erosion of rainstorm runoff and atmospheric wet and dry depositions. In the reservoir, the transport time of PAHs in the dry season was longer than that in the wet season, the stable values of isomer ratios in the wet season implied that there were continuously new inputs along the river. The estimation for the impoundment flux of PAHs revealed that water impoundment caused the 2339 kg yr^{-1} of PAHs entrapment in the SKR. These results would provide understanding of the levels, biological effects, transport and fate of PAHs in the largest hydropower reservoir of Southeast China, and also provide evidence of pollutants which can provide the information for regional water resources and ecological health protection, China.

Declaration of competing interest

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

Acknowledgments

This work was funded by National Natural Science Foundation of China (No. 41276066, 20777060). Many thanks to the Fujian Environmental Monitoring Central Station for assistance in sample collection.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.113603.

References

Audry, S., Grosbois, C., Bril, H., Schafer, J., Kierczak, J., Blanc, G., 2010. Post-depositional redistribution of trace metals in reservoir sediments of a mining/smelting-impacted watershed (the Lot River, SW France). Appl. Geochem. 25 (6), 778–794. https://doi.org/10.1016/j.apgeochem.2010.02.009.

Brown, P.H., Magee, D., Xu, Y., 2008. Socioeconomic vulnerability in China's hydropower development. China Econ. Rev. 19, 614–627. https://doi.org/10.1016/j.chieco.2008.06.002.

Campbell, C.E., Knoechel, R., Copeman, D., 1998. Evaluation of factors related to increased zooplankton biomass and altered species composition following impoundment of a Newfoundland reservoir. Can. J. Fish. Aquat. Sci. 55 (1), 230–238. https://doi.org/10.1139/f97-248.

Carls, M.G., Holland, L., Larsen, M., Collier, T.K., Scholz, N.L., Incardona, J.P., 2008. Fish embryos are damaged by dissolved PAHs, not oil particles. Aquat. Toxicol. 88 (2), 121–127. https://doi.org/10.1016/j.aquatox.2008.03.014.

Chao, B.F., Wu, Y.H., Li, Y.S., 2008. Impact of artificial reservoir water impoundment on global sea level. Science 320 (6873), 212–214. https://doi.org/10.1126/science.1154580.

Chen, Y.J., Lin, T., Tang, J.H., Xie, Z.Y., Tian, C.G., Li, J., Zhang, G., et al., 2016. Exchange of polycyclic aromatic hydrocarbons across the air-water interface in the Bohai and Yellow Seas. Atmos. Environ. 141, 153–160. https://doi.org/10.1016/j.atmosenv.2016.06.039.

Chen, X., Pan, W.B., Wang, M., 2012. Spatial distribution characteristics and dynamics of Eichhornia crassipes in the Shuikou reservoir, Fujian province. J. Lake Sci. 24, 391–399 (in Chinese).

Countway, R.E., Dickhut, R.M., Canuel, E.A., 2003. Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary. Org. Geochem. 34 (2), 209–224. https://doi.org/10.1016/S0146-6380(02)00162-6.

Dai, Z., Du, J., Zhang, X., Su, N., Li, J., 2011. Variation of riverine material loads and environmental consequences on the Changjiang (Yangtze) Estuary in recent decades (1955-2008). Environ. Sci. Technol. 45 (1), 223–227. https://doi.org/10.1021/es103026a.

Dang, T.H., Coynel, A., Orange, D., Blanc, G., Etcheber, H., Le, L.A., 2010. Long-term monitoring (1960-2008) of the river-sediment transport in the Red River Watershed (Vietnam): temporal variability and dam-reservoir impact. Sci. Total Environ. 408 (15), 4654–4664. https://doi.org/10.1016/j.scitotenv.2010.07.007.

Del Vento, S., Dachs, J., 2007. Atmospheric occurrence and deposition of polycyclic aromatic hydrocarbons in the northeast tropical and subtropical Atlantic Ocean. Environ. Sci. Technol. 41 (16), 5608–5613. https://doi.org/10.1021/es0707660.

Deyerling, D., Wang, J., Hu, W., Westrich, B., Peng, C., Bi, Y., Henkelmann, B., Schramm, K.W., 2014. PAH distribution and mass fluxes in the three Gorges reservoir after impoundment of the three Gorges dam. Sci. Total Environ. 491–492, 123–130. https://doi.org/10.1016/j.scitotenv.2014.03.076.

Du, J.J., Jing, C.Y., 2018. Anthropogenic PAHs in lake sediments: a literature review (2002-2018). Environ. Sci.: Process. Impacts 20, 1649–1666. https://doi.org/10.1039/c8em00195b.

EUC, 2013. Environmental Quality Standards Applicable to Surface Water (Directive 2013/39/EU). Official Journal of the European Union. https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:226:0001:0017:en:PDF.

Gigliotti, C.L., Totten, L.A., Offenberg, J.H., Dachs, J., Reinfelder, J.R., Nelson, E.D., Glenn IV, T.R., Eisenreich, S.J., 2005. Atmospheric concentrations and deposition of polycyclic aromatic hydrocarbons to the Mid-Atlantic East Coast Region. Environ. Sci. Technol. 39 (15), 5550–5559. https://doi.org/10.1021/es050401k.

Gonzalez-Gaya, B., Martinez-Varela, A., Vila-Costa, M., Casal, P., Cerro-Galvez, E., Berrojalbiz, N., Lundin, D., Vidal, M., Mompean, C., Bode, A., Jimenez, B., Dachs, J., 2019. Biodegradation as an important sink of aromatic hydrocarbons in the oceans. Nat. Geosci. 12, 119–125. https://doi.org/10.1038/s41561-018-0285-3.

González-Gaya, B., Zúñiga-Rival, J., Ojeda, M.J., Jiménez, B., Dachs, J., 2014. Field measurements of the atmospheric dry deposition fluxes and velocities of polycyclic aromatic hydrocarbons to the global oceans. Environ. Sci. Technol. 48 (10), 5583–5592. https://doi.org/10.1021/es500846p.

Humborg, C., Ittekkot, V., Cociasu, A., VonBodungen, B., 1997. Effect of Danube river dam on black sea biogeochemistry and ecosystem structure. Nature 386 (6623), 385–388. https://doi.org/10.1038/386385a0.

Jiang, Y., Lin, T., Wu, Z., Li, Y., Li, Z., Guo, Z., Yao, X., 2018. Seasonal atmospheric deposition and air–sea gas exchange of polycyclic aromatic hydrocarbons over the Yangtze River Estuary, East China Sea: implications for source–sink processes. Atmos. Environ. 178, 31–40. https://doi.org/10.1016/j.atmosenv.2018.01.031.

Katsoyiannis, A., Breivik, K., 2014. Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool. Environ. Pollut. 184, 488–494. https://doi.org/10.1016/j.envpol.2013.09.028.

Lang, C., Tao, S., Liu, W., Zhang, Y., Simonich, S., 2008. Atmospheric transport and outflow of polycyclic aromatic hydrocarbons from China. Environ. Sci. Technol. 42 (14), 5196–5201. https://doi.org/10.1021/es800453n.

Lang, Q., Zhang, Q., Jaffé, R., 2002. Organic aerosols in the Miami area, USA: temporal variability of atmospheric particles and wet/dry deposition. Chemosphere 47 (4), 427–441. https://doi.org/10.1016/S0045-6535(01)00318-6.

Larsen, R.K., Baker, J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environ. Sci. Technol. 37 (9), 1873–1881. https://doi.org/10.1021/es0206184.

Li, Y.X., Duan, X.Y., 2015. Polycyclic aromatic hydrocarbons in sediments of China Sea. Environ. Sci. Pollut. Res. 22 (20), 15432–15442. https://doi.org/10.1007/s11356-015-5333-6.

Li, X., Hou, L., Li, Y., Liu, M., Lin, X., Cheng, L., 2016. Polycyclic aromatic hydrocarbons and black carbon in intertidal sediments of China coastal zones: concentration, ecological risk, source and their relationship. Sci. Total Environ. 566–567, 1387–1397. https://doi.org/10.1016/j.scitotenv.2016.05.212.

Lin, L., Dong, L., Meng, X., Li, Q., Huang, Z., Li, C., Li, R., Yang, W., Crittenden, J., 2018. Distribution and sources of polycyclic aromatic hydrocarbons and phthalic acid esters in water and surface sediment from the Three Gorges Reservoir.

J. Environ. Sci. China 69, 271–280. https://doi.org/10.1016/j.jes.2017.11.004.
Lin, T., Hu, L., Guo, Z., Zhang, G., Yang, Z., 2013a. Deposition fluxes and fate of polycyclic aromatic hydrocarbons in the Yangtze River estuarine-inner shelf in the East China Sea. Glob. Biogeochem. Cycles 27 (1), 77–87. https://doi.org/10.1029/2012GB004317.
Lin, T., Qin, Y.W., Zheng, B.H., Li, Y.Y., Zhang, L., Guo, Z.G., 2012. Sedimentary record of polycyclic aromatic hydrocarbons in a reservoir in Northeast China. Environ. Pollut. 163, 256–260. https://doi.org/10.1016/j.envpol.2012.01.005.
Lin, T., Qin, Y.W., Zheng, B.H., Li, Y.Y., Chen, Y., Guo, Z.G., 2013b. Source apportionment of polycyclic aromatic hydrocarbons in the Dahuofang Reservoir, Northeast China. Environ. Monit. Assess. 185 (1), 945–953. https://doi.org/10.1007/s10661-012-2605-1.
Liu, Y., Shen, J.M., Chen, Z.L., Ren, N.Q., Li, Y.F., 2013. Distribution of polycyclic aromatic hydrocarbons in surface water and sediment near a drinking water reservoir in Northeastern China. Environ. Sci. Pollut. Res. 20, 2535–2545. https://doi.org/10.1007/s11356-012-1164-x.
Luo, X.J., Mai, B.X., Yang, Q.S., Chen, S.J., Zeng, E.Y., 2008. Distribution and partition of polycyclic aromatic hydrocarbon in surface water of the Pearl River Estuary, South China. Environ. Monit. Assess. 145 (1–3), 427–436. https://doi.org/10.1007/s10661-007-0051-2.
Mai, B., Qi, S., Zeng, E.Y., Yang, Q., Zhang, G., Fu, J., Sheng, G., Peng, P., Wang, Z., 2003. Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: assessment of input sources and transport pathways using compositional analysis. Environ. Sci. Technol. 37 (21), 4855–4863. https://doi.org/10.1021/es034514k.
Meng, Y., Liu, X.H., Lu, S.Y., Zhang, T.T., Jin, B.C., Wang, Q., Tang, Z.R., Liu, Y., Guo, X.C., Zhou, J.L., Xi, B.D., 2019. A review on occurrence and risk of polycyclic aromatic hydrocarbons (PAHs) in lakes of China. Sci. Total Environ. 651, 2497–2506. https://doi.org/10.1016/j.scitotenv.2018.10.162.
Ministry of Water Resources of the People's Republic of China, 2018. 2017 Statistic Bulletin on China Water Activities. http://www.mwr.gov.cn/sj/tjgb/slfztjgb/201811/t20181116_1055056.html.
Morais, P., Chícharo, M.A., Chícharo, L., 2009. Changes in a temperate estuary during the filling of the biggest European dam. Sci. Total Environ. 407 (7), 2245–2259. https://doi.org/10.1016/j.scitotenv.2008.11.037.
Mwanamoki, P.M., Devarajan, N., Thevenon, F., Birane, N., de Alencastro, L.F., Grandjean, D., Mpiana, P.T., Prabakar, K., Mubedi, J.I., Kabele, C.G., Wildi, W., Pote, J., 2014. Trace metals and persistent organic pollutants in sediments from river-reservoir systems in Democratic Republic of Congo (DRC): spatial distribution and potential ecotoxicological effects. Chemosphere 111, 485–492. https://doi.org/10.1016/j.chemosphere.2014.04.083.
Ngabe, B., Bidleman, T.F., Scott, G.I., 2000. Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina. Sci. Total Environ. 255 (1–3), 1–9. https://doi.org/10.1016/S0048-9697(00)00422-8.
Prokeš, R., Vrana, B., Klánová, J., 2012. Levels and distribution of dissolved hydrophobic organic contaminants in the Morava river in Zlín district, Czech Republic as derived from their accumulation in silicone rubber passive samplers. Environ. Pollut. 166, 157–166. https://doi.org/10.1016/j.envpol.2012.02.022.
Qin, N., He, W., Kong, X.Z., Liu, W.X., He, Q.S., Yang, B., Ouyang, H.L., Wang, Q.M., Xu, F.L., 2013. Atmospheric partitioning and the air-water exchange of polycyclic aromatic hydrocarbons in a large shallow Chinese lake (Lake Chaohu). Chemosphere 93, 1685–1693. https://doi.org/10.1016/j.chemosphere.2013.05.038.
Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42 (13), 2895–2921. https://doi.org/10.1016/j.atmosenv.2007.12.010.
Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. Environ. Toxicol. Chem. 25 (5), 1239–1245. https://doi.org/10.1897/05-458R.1.
Ren, Y., Zhou, B., Tao, J., Cao, J., Zhang, Z., Wu, C., Wang, J., Li, J., Zhang, L., Han, Y., Liu, L., Cao, C., Wang, G., 2017. Composition and size distribution of airborne particulate PAHs and oxygenated PAHs in two Chinese megacities. Atmos. Res. 183, 322–330. https://doi.org/10.1016/j.atmosres.2016.09.015.
Rosenberg, D.M., McCully, P., Pringle, C.M., 2000. Global-scale environmental effects of hydrological alterations: introduction. Bioscience 50 (9), 746–751. https://doi.org/10.1641/0006-3568(2000)050[0746:GSEEOH]2.0.CO;2.
Salim, I., Sajjad, R.U., Paule-Mercado, M.C., Memon, S.A., Lee, B.Y., Sukhbaatar, C., Lee, C.H., 2019. Comparison of two receptor models PCA-MLR and PMF for source identification and apportionment of pollution carried by runoff from catchment and sub-watershed areas with mixed land cover in South Korea. Sci. Total Environ. 663, 764–775. https://doi.org/10.1016/j.scitotenv.2019.01.377.
SEPA of China, 2002. Environment Quality Standard for Surface Water, GB3838–2002. http://kjs.mee.gov.cn/hjbhbz/bzwb/shjbh/shjzlbz/200206/W020061027509896672057.pdf.
Sun, Y., Qi, S.H., Li, H., Huang, H.F., Yang, D., Fan, Y.H., Min, Y., Qu, C.K., 2016. Concentrations, sources and health risk assessment of polycyclic aromatic hydrocarbons in soils collected along the banks of Minjiang River, Fujian, China. China Environ. Sci. 36 (6), 1821–1829 (in Chinese).
Tian, Y.Z., Li, W.H., Shi, G.L., Feng, Y.C., Wang, Y.Q., 2013. Relationships between PAHs and PCBs, and quantitative source apportionment of PAHs toxicity in sediments from Fenhe reservoir and watershed. J. Hazard Mater. 248, 89–96. https://doi.org/10.1016/j.jhazmat.2012.12.054.
Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119. https://doi.org/10.1016/j.envpol.2011.10.025.
Tsapakis, M., Stephanou, E.G., Karakassis, I., 2003. Evaluation of atmospheric transport as a nonpoint source of polycyclic aromatic hydrocarbons in marine sediments of the Eastern Mediterranean. Mar. Chem. 80, 283–298. https://doi.org/10.1016/S0304-4203(02)00132-9.
US EPA, 2015. National Recommended Water Quality Criteria-Human Health Criteria. https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table.
Vörösmarty, C.J., Meybeck, M., Fekete, B., Sharma, K., Green, P., Syvitski, J.P.M., 2003. Anthropogenic sediment retention: major global impact from registered river impoundments. Glob. Planet. Chang. 39 (1–2), 169–190. https://doi.org/10.1016/S0921-8181(03)00023-7.
Wang, J.Z., Guan, Y.F., Ni, H.G., Luo, X.L., Zeng, E.Y., 2007. Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): concentrations, fluxes, and fate. Environ. Sci. Technol. 41 (6), 5614–5619. https://doi.org/10.1021/es070964r.
Wang, J.X., Bi, Y.H., Henkelmann, B., Pfister, G., Zhang, L., Schramm, K.-W., 2016. PAHs and PCBs accumulated by SPMD-based virtual organisms and feral fish in Three Gorges Reservoir, China. Sci. Total Environ. 542 (Part A), 899–907. https://doi.org/10.1016/j.scitotenv.2015.10.134.
Wang, J.X., Henkelmann, B., Bi, Y.H., Zhu, K.X., Pfister, G., Hu, W., Temoka, C., Westrich, B., Schramm, K.-W., 2012. Temporal variation and spatial distribution of PAH in water of Three Gorges Reservoir during the complete impoundment period. Environ. Sci. Pollut. Res. 20 (10), 7071–7079. https://doi.org/10.1007/s11356-012-1427-6.
Wang, J.X., Bi, Y.H., Pfister, G., Henkelmann, B., Zhu, K.X., Schramm, K.W., 2009. Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). Chemosphere 75 (8), 1119–1127. https://doi.org/10.1016/j.chemosphere.2009.01.016.
Wang, X.T., Chu, S.G., Ma, L.L., Sun, Y.Z., Li, X.H., Xu, X.B., 2004. Contamination of priority polycyclic aromatic hydrocarbons in water from Guanting reservoir and the Yongding River, China. Bull. Environ. Contam. Toxicol. 72 (1), 194–201. https://doi.org/10.1007/s00128-003-0259-y.
Wei, X., Han, L.F., Gao, B., Zhou, H.D., Lu, J., Wan, X.H., 2016. Distribution, bioavailability, and potential risk assessment of the metals in tributary sediments of Three Gorges Reservoir: the impact of water impoundment. Ecol. Indicat. 61, 667–675. https://doi.org/10.1016/j.ecolind.2015.10.018.
Wu, J., Huang, J., Han, X., Gao, X., He, F., Jiang, M., Jiang, Z., Primack, R.B., Shen, Z., 2004. The three Gorges dam: an ecological perspective. Front. Ecol. Environ. 2 (5), 241–248. https://doi.org/10.1890/1540-9295(2004)002[0241:TTGDAE]2.0.CO;2.
Wu, X., Wang, Y., Zhang, Q., Zhao, H., Yang, Y., Zhang, Y., Xie, Q., Chen, J., 2019. Seasonal variation, air-water exchange, and multivariate source apportionment of polycyclic aromatic hydrocarbons in the coastal area of Dalian, China. Environ. Pollut. 244, 405–413. https://doi.org/10.1016/j.envpol.2018.10.075.
Wu, Y.L., Wang, X.H., Li, Y.Y., Hong, H.S., 2011. Occurrence of polycyclic aromatic hydrocarbons (PAHs) in seawater from the Western Taiwan Strait, China. Mar. Pollut. Bull. 63 (5–12), 459–463. https://doi.org/10.1016/j.marpolbul.2011.03.008, 2011.
Xu, Y., Sun, Q., Yi, L., Yin, X., Wang, A., Li, Y., Chen, J., 2014. The source of natural and anthropogenic heavy metals in the sediments of the Minjiang River Estuary (SE China): implications for historical pollution. Sci. Total Environ. 493, 729–736. https://doi.org/10.1016/j.scitotenv.2014.06.046.
Xu, S., Liu, W., Tao, S., 2006. Emission of polycyclic aromatic hydrocarbons in China. Environ. Sci. Technol. 40 (3), 702–708. https://doi.org/10.1021/es0517062.
Ya, M.L., Wu, Y.L., Li, Y.Y., Wang, X.H., 2017a. Transport of terrigenous polycyclic aromatic hydrocarbons affected by the coastal upwelling in the northwestern coast of South China Sea. Environ. Pollut. 229, 60–68. https://doi.org/10.1016/j.envpol.2017.05.054.
Ya, M.L., Wang, X.H., Wu, Y.L., Li, Y.Y., Yan, J.M., Fang, C., Zhao, Y.Y., Qian, R.R., Lin, X.L., 2017b. Seasonal variation of terrigenous polycyclic aromatic hydrocarbons along the marginal seas of China: input, phase partitioning, and ocean-current transport. Environ. Sci. Technol. 51 (16), 9072–9079. https://doi.org/10.1021/acs.est.7b02755.
Ya, M.L., Xu, L., Wu, Y.L., Li, Y.Y., Zhao, S.H., Wang, X.H., 2018. Fossil fuel-derived polycyclic aromatic hydrocarbons in the Taiwan Strait, China, and fluxes across the air–water interface. Environ. Sci. Technol. 52 (13), 7307–7316. https://doi.org/10.1021/acs.est.8b01331.
Yang, B., Zhou, L.L., Xue, N.D., Li, F.S., Li, Y.W., Vogt, R.D., Cong, X., Yan, Y.Z., Liu, B., 2013. Source apportionment of polycyclic aromatic hydrocarbons in soils of Huanghuai Plain, China: comparison of three receptor models. Sci. Total Environ. 443, 31–39. https://doi.org/10.1016/j.scitotenv.2012.10.094.
Yu, K.S.H., Wong, A.H.Y., Yau, K.W.Y., Wong, Y.S., Tam, N.F.Y., 2005. Natural attenuation, biostimulation and bioaugmentation on biodegradation of polycyclic aromatic hydrocarbons (PAHs) in mangrove sediments. Mar. Pollut. Bull. 51 (8–12), 1071–1077. https://doi:10.1016/j.marpolbul.2005.06.006.
Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33 (4), 489–515. https://doi.org/10.1016/S0146-6380(02)00002-5.
Zhang, K., Liang, B., Wang, J.Z., Guan, Y.F., Zeng, E.Y., 2012. Polycyclic aromatic hydrocarbons in upstream riverine runoff of the Pearl River Delta, China: an assessment of regional input sources. Environ. Pollut. 167, 78–84. https://

doi.org/10.1016/j.envpol.2012.03.049.
Zhang, Z., Hong, H., Zhou, J., Yu, G., 2004. Phase association of polycyclic aromatic hydrocarbons in the Minjiang River Estuary, China. Sci. Total Environ. 323 (1–3), 71–86. https://doi.org/10.1016/j.scitotenv.2003.09.026.
Zhu, L., Chen, B., Wang, J., Shen, H., 2004. Pollution survey of polycyclic aromatic hydrocarbons in surface water of Hangzhou, China. Chemosphere 56 (11), 1085–1095. https://doi.org/10.1016/j.chemosphere.2004.05.025.